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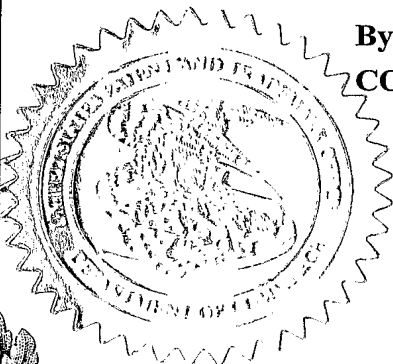
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INVENTOR(S)					
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<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (280 characters max)					
A SWITCHABLE SELF-DOPED POLYANILINE					
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification		Number of Pages	13	<input type="checkbox"/> CD(s), Number	
<input checked="" type="checkbox"/> Drawing(s)		Number of Sheets	3	<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
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Respectfully submitted,

SIGNATURE

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03/12/03

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## A SWITCHABLE SELF-DOPED POLYANILINE

### FIELD OF THE INVENTION

The present invention relates generally to the field of polymers and  
5 polymer chemistry. More specifically, the present invention relates to a switchable  
self-doped polyaniline and its interconversion between self-doped and non-self-doped  
forms.

### BACKGROUND OF THE INVENTION

10 Polyaniline, one of the most promising intrinsically conducting polymers,  
has received considerable attention in recent years due to its straightforward  
polymerization, chemical stability, relatively high conductivity and potential  
applications in electronic devices, batteries and sensors. A major breakthrough in the  
field was the discovery of self-doped polyaniline due to its desirable properties. For  
15 example, the self-doped form of polyaniline has several advantages including better  
solubility as well as redox activity and conductivity over a wider pH range. However,  
there are a number of tradeoffs including reduced mechanical stability (especially in  
the presence of good solvents) and decreased conductivity due to steric effects.  
Ideally, it should be possible to switch between self-doped and non-self-doped states  
20 so that the properties of the polymer can be manipulated to achieve desired  
properties during synthesis, processing, and finally use of the polymer.

Herein we report a novel approach to the creation of a substituted  
polyaniline whose self-doped state can be controlled via complexation between

boronic acid groups along the backbone with D-fructose in the presence of fluoride. For the first time, this allows the formation of a water-soluble, self-doped conducting polymer under the polymerization conditions. In turn this facilitates the growth of polyaniline over a wider pH range. This has important implications toward synthesis (yield, molecular weight), processing (controlled precipitation), and implementation (extended pH range).

### SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided a self-doped polyaniline capable of converting between:

a water-soluble self-doped form comprising repeating units as shown in (2) of Figure 1; and

a water-insoluble non-self-doped form comprising repeating units as shown in (1) of Figure 1,

wherein the water-soluble form is converted to the water-insoluble form by reducing fluoride concentration of the polymer.

According to a second aspect of the invention, there is provided a method of making a self-doped polyaniline comprising:

(a) providing monomer (1), D-fructose and fluoride;

(b) incubating the monomer (1), the D-fructose and the fluoride under conditions suitable for polymerization, thereby producing polymer (2);

(c) precipitating the polymer (2) by reducing the fluoride concentration, thereby producing polymer (1).

According to a third aspect of the invention, there is provided a polymer capable of converting between a self-doped form and a non-self doped form by a reversible chemical reaction. In the examples described herein, the polymer is polyaniline and the reactive components are boronic acid, D-fructose and fluoride. As  
5 will be appreciated by one of skill in the art, other suitable polymers, substituents and reactive components may also be used within the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows the structure of the monomer (1) and the boronate  
10 ester thereof (2).

FIGURE 2 shows the UV-vis spectral changes of a poly(2) thin film as a function of time upon exposure to pH 7.4 phosphate-buffered saline over the course of an hour.

FIGURE 3 shows the IR spectra of (a) poly(2) and (b) poly(1).

15 FIGURE 4 shows the cyclic voltammograms of (a) an electrochemically deposited film and (b) a film cast from precipitate of poly(1) on glassy carbon in 0.5 M HCl at a scan rate of  $100 \text{ mV s}^{-1}$ .

FIGURE 5 shows GPC chromatographs for 0.033 mg/ml of poly(1) (solid line) and poly(2) (dashed line) dissolved in NMP.

20

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to

which the invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. All publications mentioned hereunder are incorporated herein by reference.

5           Herein we report a novel approach to the creation of a substituted polyaniline whose self-doped state can be controlled via complexation between boronic acid groups along the backbone with D-fructose in the presence of fluoride. For the first time, this allows the formation of a water-soluble, self-doped conducting polymer under the polymerization conditions. In turn this facilitates the growth of polyaniline  
10 over a wider pH range. This has important implications toward synthesis (yield, molecular weight), processing (controlled precipitation), and implementation (extended pH range).

As will be known to one of skill in the art, the prior art teaches polyaniline and other self-doped polyanilines having low molecular weights on the order of 10's of  
15 thousands. In a very few cases, polymers have been made having higher molecular weights approaching one million. However, the method of producing these polymers is very tedious and results in low yields. This is in contrast with the instant invention, wherein polymers having molecular weights on the order of a million or more are produced with high yields.

20           Described herein are exemplary examples for preparation of the polymer. However, as will be apparent to one of skill in the art, any suitable concentration range, ratio, oxidant and/or temperature that is known in the literature may be used in the instant invention.

The complexation of saccharides with aromatic boronic acids is pH dependent and can result in a neutral or anionic ester depending on solution conditions. Addition of fluoride can be used to enhance the complexation of saccharides under less basic conditions and facilitates the formation of an anionic ester. Under neutral pH  
5 conditions in the presence of excess D-fructose (10 M) and one equivalent of fluoride,  $^{11}\text{B}$  NMR indicates that the monomer (1) is converted to a boronate ester (2) (both shown in Figure 1) which can in turn form the basis of a self-doped polyaniline.

The requirement as shown in prior art is that an anionic species be covalently attached along the backbone of the polymer. The first demonstration used  
10 concentrated sulphuric acid to react with polyaniline resulting in a sulfonated backbone. The degree of sulfonation (i.e., the percent of the repeat units that had a sulfonate on it) was ill-defined. In subsequent work, people have shown other anions that can be attached on the backbone.

Oxidative polymerization of (2) was carried out under ambient conditions with  
15 the addition of ammonium persulfate, resulting in a water soluble, self-doped polymer (vide infra). Poly(2) was precipitated by reducing the fluoride concentration via dilution. Following filtering and rinsing with water, the precipitate could be redissolved in an aqueous solution containing the original D-fructose and fluoride concentrations.

The UV-vis spectra of the soluble form of poly(2), shown in Figure 2, (in the  
20 presence of D-fructose and fluoride) as well as thin films of the precipitated form of poly(2) are similar to those of the emeraldine salt form of unsubstituted polyaniline, exhibiting absorption bands near 350 nm and 820 nm due to the  $\pi$ - $\pi^*$  and bipolaron band transitions respectively. The existence of these bands in pure water suggests



that poly(2) exists in a self-doped state.

Poly(2) was converted to poly(1) by the removal of D-fructose from the polymer in phosphate buffer saline solution. The conversion to the non-self-doped state and subsequently to the emeraldine base form of the polymer is characterized by the appearance of an absorption band at 600 nm and the disappearance of the peak at 820 nm as shown in Figure 2. The switching behavior is reversible by exposing the base form of poly(1) to the original concentrations of D-fructose and fluoride either in phosphate buffer saline or pure water.

Switching between the self-doped and non-self-doped state is further supported by IR spectra and elemental analysis. The IR spectra of poly(2) and poly(1) are shown in Figure 3. Characteristic IR bands attributed to the poly(2) form occur at 1597, 1462, 1353, 1230, 1140, 921, 812 and 780  $\text{cm}^{-1}$ . The ratio of the relative intensities of quinoid to benzenoid ring modes ( $I_{1597} / I_{1462}$ ) clearly shows that the percentage of imine units is higher than amine units and the polymer is therefore in its conductive self-doped form. The band at 1063  $\text{cm}^{-1}$  is attributed to C-O stretching and bending modes in the D-fructose moiety. Following conversion to poly(1) the spectra exhibits reduced intensity for all bands, which is consistent with the emeraldine base form of polyaniline and is due to charge carrier motion connected with lower conductivity of the polymer. The disappearance of the 1063  $\text{cm}^{-1}$  band further supports the conclusion that D-fructose is removed from the polymer to form poly(1) in a non-self-doped state.

Elemental analysis of the two forms of the polymer is consistent with the UV-vis and IR results. Atomic ratios of the poly(2) confirmed the presence of somewhat more

than one equivalent of D-fructose bound to the boronic acid group on the backbone (C:N:O: theoretical-12:1:6 and experimental-16:1:11). In the case of poly(1), the atomic ratios (C:N:O; theoretical-6:1:2 and experimental-6:1:2) are similar to that of the uncomplexed monomer, indicating that D-fructose is no longer present in the polymer and that it is therefore in a non-self-doped state.

Thin films of poly(2) that had been converted to poly(1) exhibit electrochemical behavior similar to films of poly(1) deposited electrochemically under acidic conditions in the presence of fluoride alone (see Figure 4). In addition, the redox behavior is similar to that observed for unsubstituted polyaniline which shows two sets of redox peaks at ~ 0.18 and 0.74 V, suggesting facile conversion between oxidation states. Consequently, it appears that polymerization under the conditions reported herein has no detrimental influence on the electronic properties of the polymer.

Since poly(2) is soluble under the reported polymerization conditions, it was not expected to suffer from effective termination of polymerization resulting from precipitation and in turn the limited molecular weight observed for polyaniline. Gel permeation chromatography of poly(1) and poly(2) in N-methylpyrrolidone was performed to determine the molecular weight of the polymers produced. Poly(1) and poly(2) exhibited single chromatographic peaks with weight-average molecular weights of 2.2 and 1.9 million respectively and polydispersities of approximately 1.2 in both cases.

In conclusion, a novel substituted polyaniline has been synthesized with the unique ability to switch between a self-doped and a non-self-doped state. In its self-doped state, the polymer is soluble under the polymerization conditions and can be

easily and reversibly converted into the insoluble non-self doped form. The ability to take advantage of the properties of both states of the polymer allows unprecedented control over the polymer during synthesis, processing and utilization.

Here the novelty lies in the ability to process (solubility), to obtain higher  
5 molecular weights and the ability to reverse the self-doped process, yielding to higher conductivity more limited solubility as discussed above.

As will be appreciated by one of skill in the art, the above described polymers may be used in any suitable application, for example, electronics, energy storage, catalysis, chemical sensing and biochemistry.

10 The invention will now be explained by way of examples. It is to be understood however that the examples are for illustrative purposes only.

3-Aminophenylboronic acid hydrochloride salt, D-fructose and ammonium persulfate were purchased from Aldrich Chemical Inc. Sodium fluoride and pH 7.4 phosphate buffer saline stock solution (10X), were purchased from Fisher Scientific.  
15 Bulk distilled water was first filtered and ion exchanged to yield 18.3 MΩ quality water using an EasyPure RF, Barnstead Thermolyne Model 7031.

*Preparation of Poly(2).* Water soluble poly(2) in the presence of D-fructose and fluoride was synthesized as follows: aqueous 40 mM ammonium persulfate (0.5 ml, oxidizing agent) was slowly added over a period of 10 min to an aqueous mixture  
20 (19.5 ml) of 40 mM 3-aminophenylboronic acid, 40 mM sodium fluoride and 10 M D-fructose. The pH of the reaction mixture was 7 before adding oxidizing agent. The mixture was stirred overnight at room temperature. In a similar manner poly(2) could also be prepared in phosphate buffer saline solution (pH 7.4). The water soluble

poly(2) formed using both methods was easily passed through a 0.02  $\mu\text{m}$  Anotop filter (Whatman). The polymer produced under these conditions was readily precipitated by diluting the solution ( $\sim 3\text{X}$  volume with pure water) and in turn reducing the fluoride concentration. The resulting precipitate was redispersed in water and centrifuged  
5 more than 20 times to remove the excess D-fructose and reactants.

Characterization. UV-vis spectra were obtained using an Agilent 8453 spectrophotometer. Cyclic voltammetric measurements were performed using a CH Instrument CHI-660 workstation controlled by a PC. A three electrode cell was used, which consisted of a glassy carbon disk working electrode (Bioanalytical Systems,  
10 3.0-mm diameter), a platinum coil auxiliary electrode, and a Ag/AgCl reference electrode. Cyclic voltammograms were conducted in a 0.5 M HCl aqueous solution with a scan rate of  $100\text{ mV}\cdot\text{s}^{-1}$ . Infrared spectra were obtained using a Bomem FT-IR spectrometer (Hartmann and Braun). Polymer samples were mixed with KBr powder to prepare pellets for IR measurements.  $^{11}\text{B}$  NMR studies were carried out using a  
15 Bruker AMX 500 NMR spectrophotometer. The monomer samples used for NMR measurements were prepared using 10%  $\text{D}_2\text{O}$  in phosphate buffer saline solution (pH 7.4). Monomer sample preparation details are given in Table 1. Elemental analyses were carried out by Chemisar Laboratories Inc.

Molecular weight was determined with gel permeation chromatography (GPC)  
20 using polystyrene standards to calibrate the column in NMP (see Figure 5). A Polymer Laboratories Inc. PLgel 5  $\mu\text{m}$  MIXED-C column was used, operating at  $70^\circ\text{C}$ . The concentration of the polymer samples were 0.033 mg/ml. A MiniDAWN Tristar detector (Wyatt Technology), operating at 690 nm, was used as the absorbance

detector. Prior to GPC experiments the polymers were dissolved in NMP with constant stirring for 48 h and filtered through a 0.02  $\mu\text{m}$  Anotop filter.

While the preferred embodiments of the invention have been described above, it will be recognized and understood that various modifications may be made  
5 therein, and the appended claims are intended to cover all such modifications which may fall within the spirit and scope of the invention.

Table 1.  $^{11}\text{B}$  NMR chemical shifts of 3-aminophenylboronicacid (3-APBA) adducts

Solution Conditions	$^{11}\text{B}$ chemical shift (ppm)
40 mM 3-APBA (pH=7.4)	29.2
40 mM 3-APBA + 40 mM NaF + 10 M Fructose (pH 7.4)	6.4

5 Shifts measured relative to reference borontrifluoride etherate

CLAIMS

1. A polymer capable of converting between a self-doped form and a non-self doped form by a reversible chemical reaction.

2. A self-doped polyaniline capable of converting between:

5 a water-soluble self-doped form comprising repeating units as shown in (2) of Figure 1; and

a water-insoluble non-self-doped form comprising repeating units as shown in (1) of Figure 1,

10 wherein the water-soluble form is converted to the water-insoluble form by reducing fluoride concentration of the polymer.

3. A method of making a self-doped polyaniline comprising:

(a) providing monomer (1), D-fructose and fluoride;

(b) incubating the monomer (1), the D-fructose and the fluoride under conditions suitable for polymerization, thereby producing polymer (2);

15 (c) precipitating the polymer (2) by reducing the fluoride concentration, thereby producing polymer (1).

ABSTRACT

A substituted polyaniline whose self-doped state can be controlled via complexation between boronic acid groups along the backbone with D-fructose in the presence of fluoride is described. For the first time, this allows the formation of a water-soluble, self-doped conducting polymer under the polymerization conditions. In turn this facilitates the growth of polyaniline over a wider pH range.



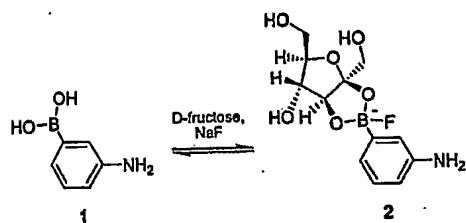


FIGURE 1

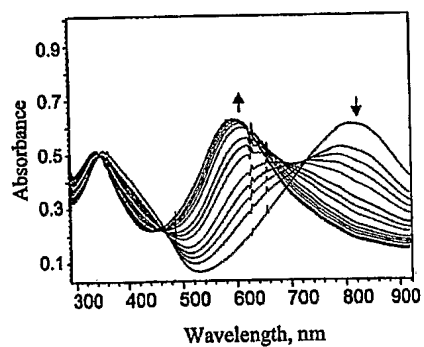


FIGURE 2

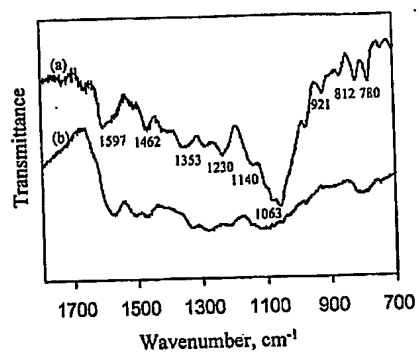


FIGURE 3

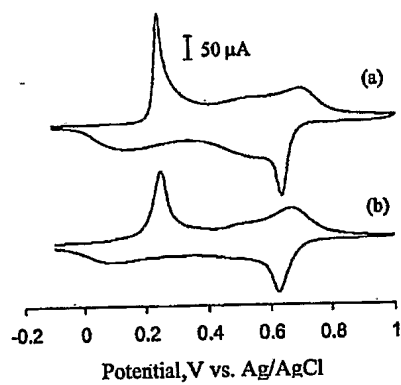


FIGURE 4

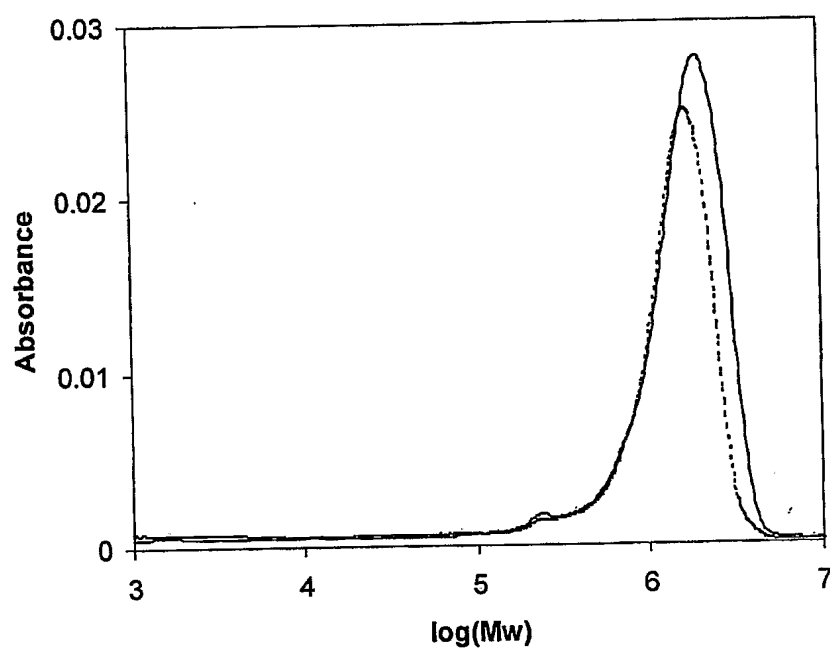


FIGURE 5